SAND2019-12705C

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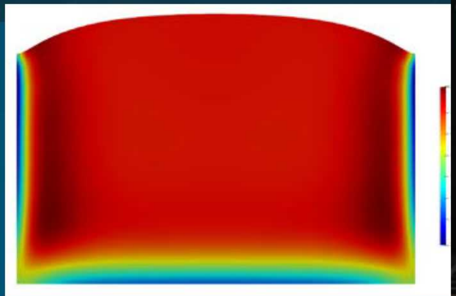
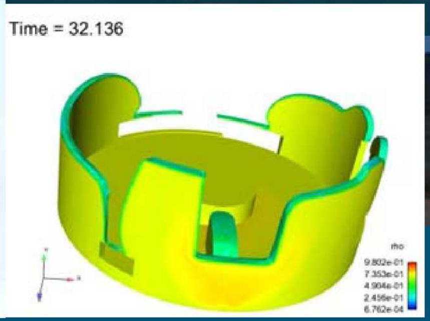
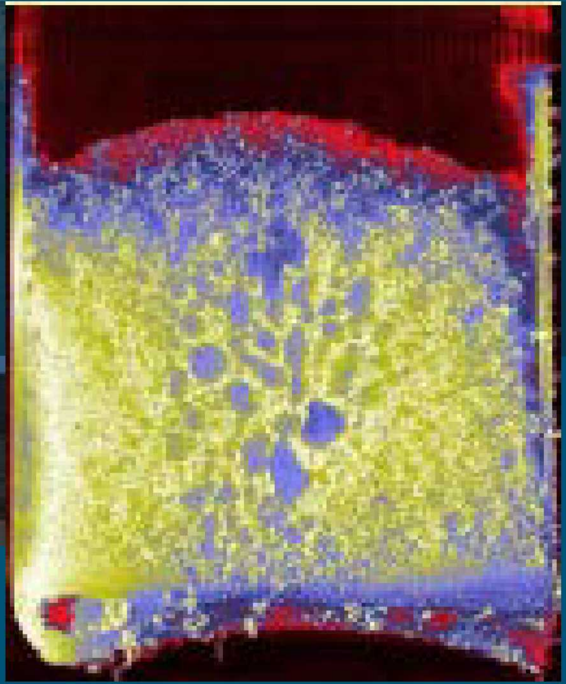
Bubble-size Predictions for Polyurethane Foam using a Population Balance Equation





PRESENTED BY

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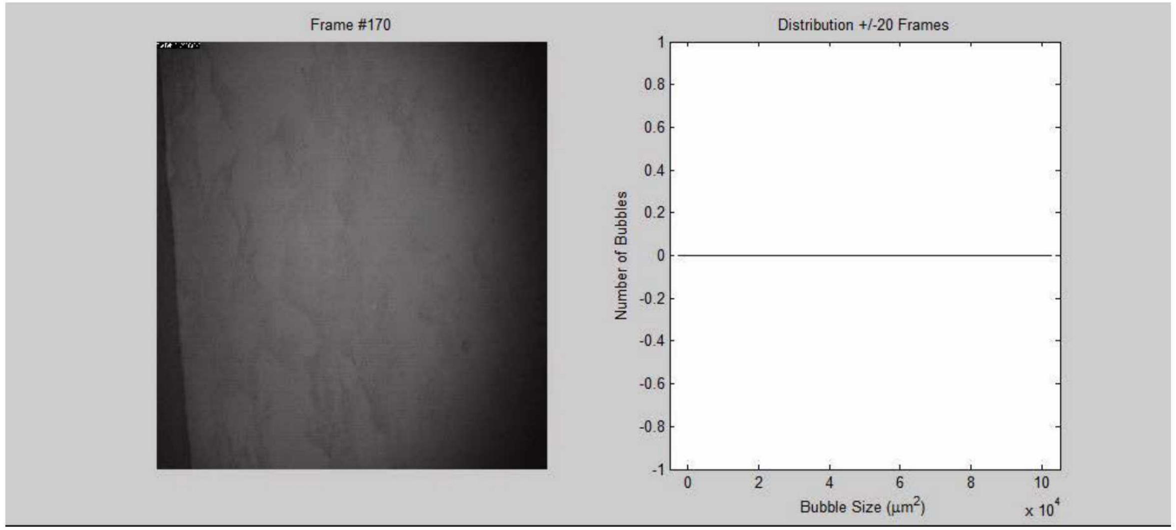
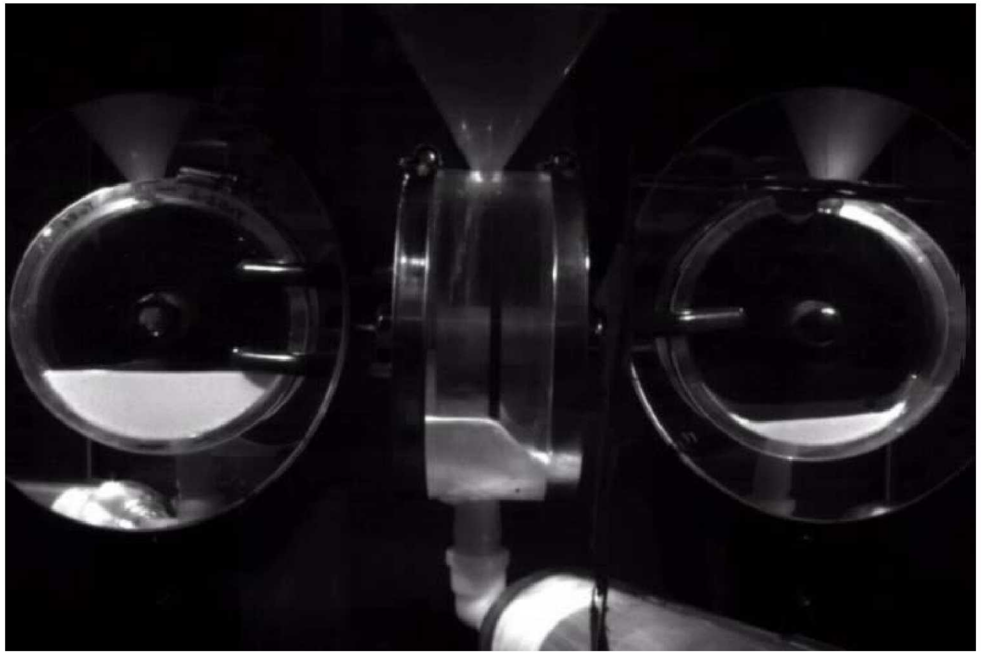
Polyurethane foams are widely used in manufacturing due to ease of use and useful material properties

We are developing models that can predict foam mold filling, void location, and final properties including density and modulus for structural foams and thermal conductivity for insulating material.

Foam Filling is Complex



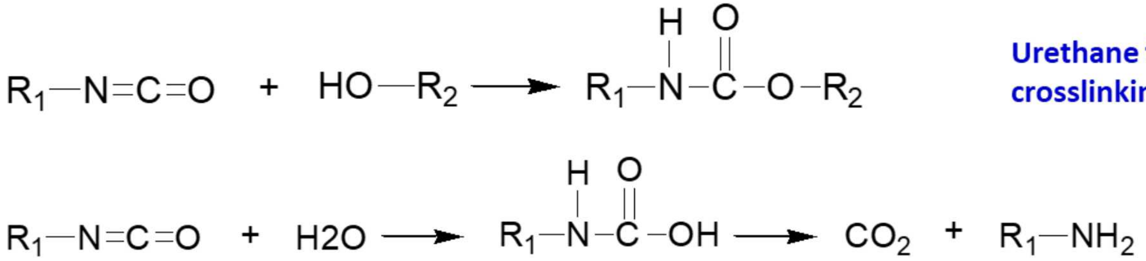
Foam front moving past camera, with bubble sizes at transparent wall determined with image processing.



3 views of foam filling with several plates spaced unevenly. Vent location is critical to keep from trapping air.

- Gas generation drives the foam expansion, changing the material from a viscous liquid to a multiphase material.
- Continuous phase is time- and temperature-dependent and eventually vitrifies to a solid.

Two key reactions: Isocyanate reaction with polyols and water



Urethane formation, crosslinking

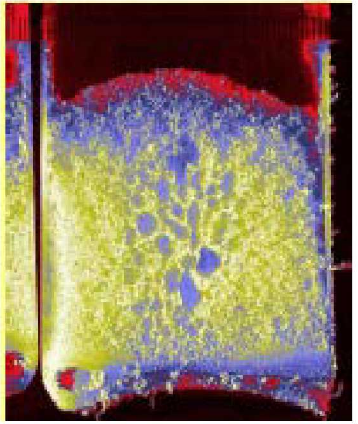
Foaming reaction yields CO_2 and amine

Equations of Motion Include Evolving Material Models

Momentum equation and continuity have variable density, shear viscosity, and bulk viscosity

$$\rho \frac{\partial \mathbf{v}}{\partial t} = -\rho \mathbf{v} \bullet \nabla \mathbf{v} - \nabla p + \nabla \bullet (\mu_f (\nabla \mathbf{v} + \nabla \mathbf{v}^t)) - \nabla \bullet \lambda (\nabla \bullet \mathbf{v}) I + \rho \mathbf{g}$$

$$\frac{D\rho_f}{Dt} + \rho_f \nabla \bullet \mathbf{v} = 0$$



NMR imaging shows coarse microstructure (Altobelli, 2006)

Energy equation has variable heat capacity and thermal conductivity including a source term for heat of reaction for foaming and curing reactions

$$\rho C_{pf} \frac{\partial T}{\partial t} + \rho C_{pf} v \bullet \nabla T = \nabla \bullet (k \nabla T) + \rho \varphi_e \Delta H_{rxn} \frac{\partial \xi}{\partial t}$$

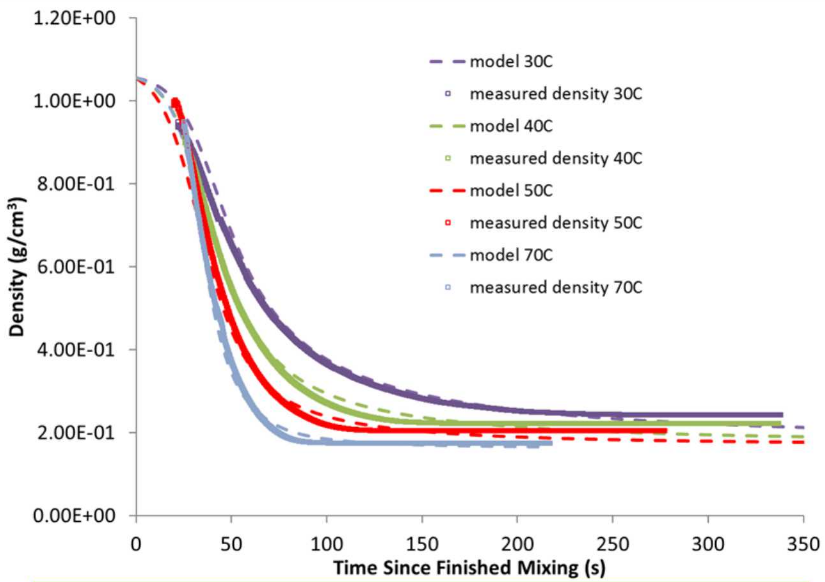
Extent of reaction equation for polymerization: condensation chemistry

$$\frac{\partial \xi}{\partial t} = \left(\frac{1}{(1+wa)^{\beta}} \right) \left(k_0 \exp\left(-\frac{E}{RT} \right) \right) \left(b + \xi^m \right) (1-\xi)^n$$

Molar concentration equations for water and carbon dioxide

$$\frac{dC_{H_2O}}{dt} = -k_{H_2O} C_{H_2O}^n \qquad C_{H_2O} = \frac{\rho_{foam} x_{H_2O}}{M_{H_2O}} \qquad k_{H_2O} = A_{H_2O} \exp(-E_{H_2O} / RT)$$

$$\frac{dC_{CO_2}}{dt} = +k_{H_2O} C_{H_2O}^n \qquad C_{CO_2} = \frac{\rho_{foam} x_{CO_2}}{M_{CO_2}}$$



Experiments to determine foaming and curing kinetics as well as parameters for model

Rao et al., "Polyurethane kinetics for foaming and polymerization" , *AICHE Journal*, 2017

Complex Material Models Vary with Cure, Temperature, and Gas Fraction

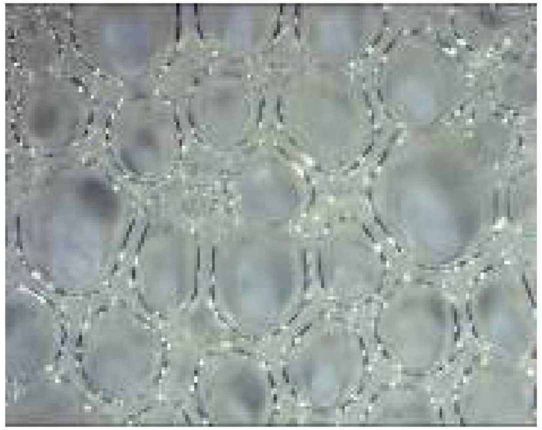
Foaming reaction predicts moles of gas from which we can calculate density

$$\rho_{gas} = \frac{PM_{CO_2}}{RT}$$

$$v = \frac{V_{gas}}{V_{liq}} = \frac{M_{CO_2} C_{CO_2}}{\rho_{gas}} \qquad \phi_v = \frac{v}{1+v}$$

$$\rho_{foam} = \rho_{gas}\phi_v + \rho_{liq}(1-\phi_v)$$

Compressibility built into this model via the ideal gas law for gas density



Foam is a collection of bubbles in curing polymer

Thermal properties depend on gas volume fraction and polymer properties

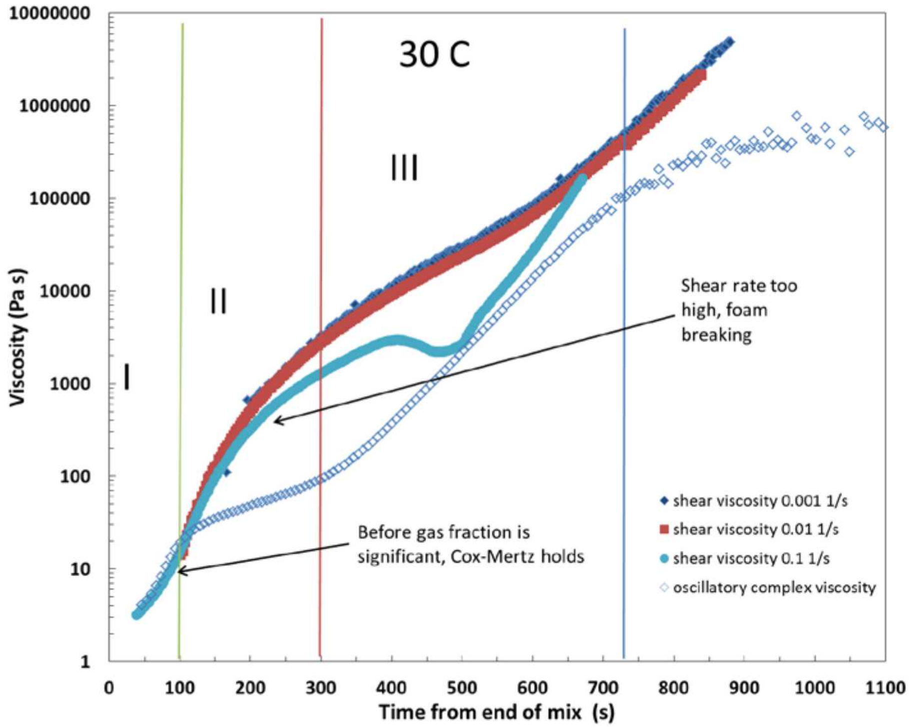
$$k = \frac{2}{3}\left(\frac{\rho}{\rho_e}\right)k_e + \left(1-\frac{\rho}{\rho_e}\right)k_v$$

$$C_{pf} = C_{pl}\phi_l + C_{pv}\phi_v + C_{pe}\phi_e$$

- Experiments to determine foaming and curing kinetics as well as parameters for model

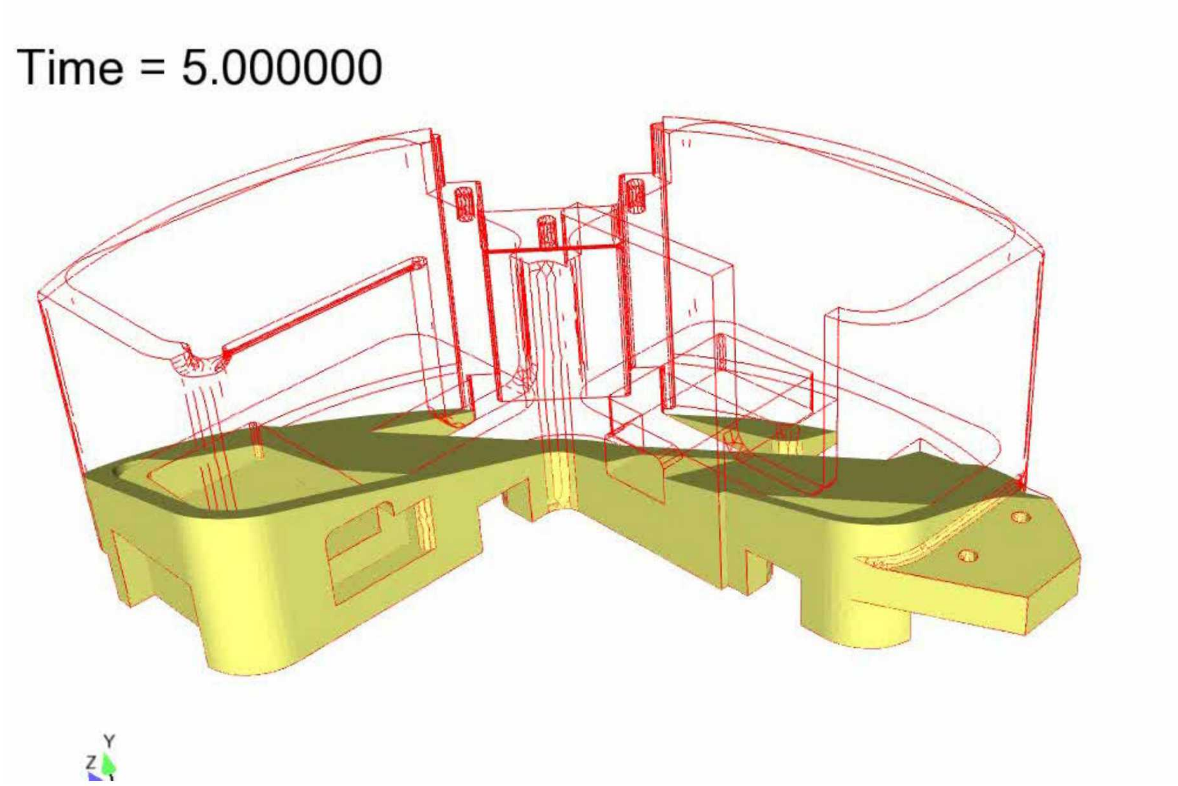
Shear and bulk viscosity depends on gas volume fraction, temperature and degree of cure

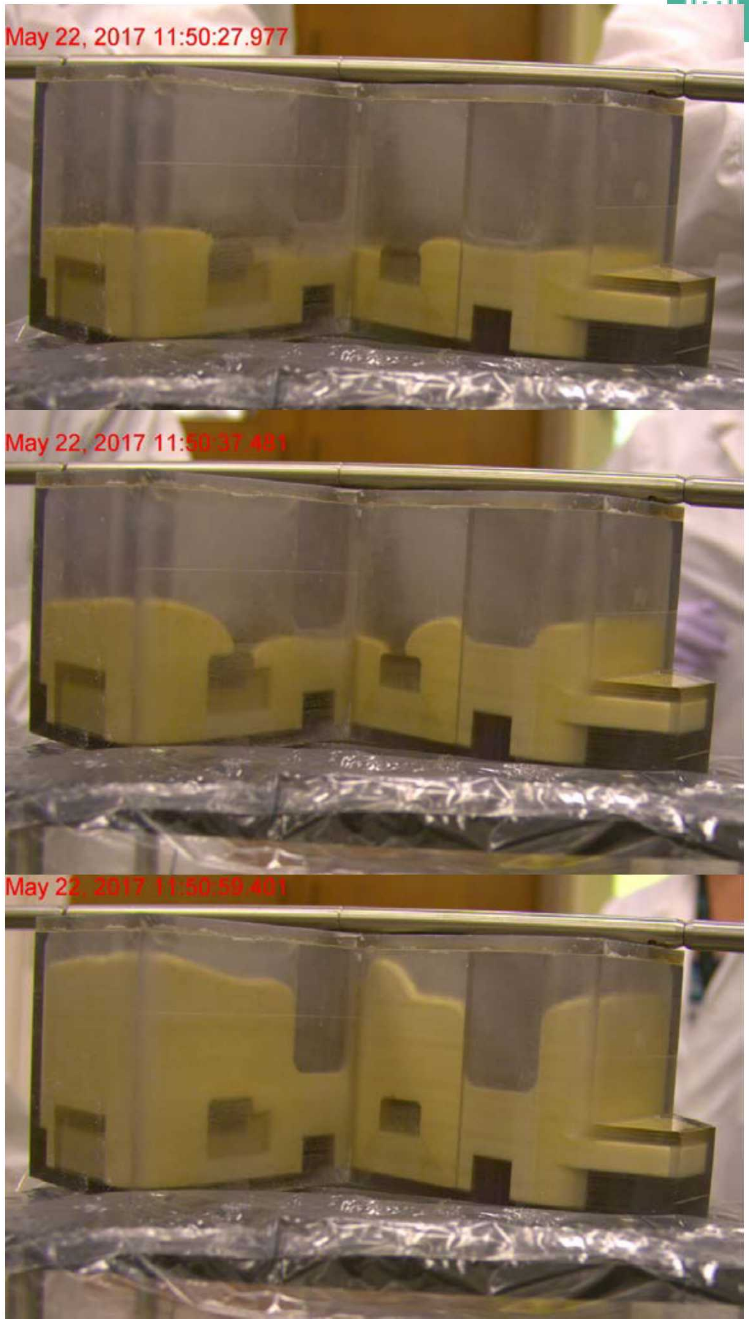
$$\mu = \mu_0 \exp\left(\frac{\varphi_v}{1-\varphi_v}\right) \quad \mu_0 = \mu_0^0 \exp\left(\frac{E_\mu}{RT}\right)\left(\frac{\xi_c^p - \xi^p}{\xi_c^p}\right)^{-q} \qquad \lambda = \frac{4}{3}\mu_0 \frac{(\phi_v - 1)}{\phi_v}$$



M. Mooney, *J. Colloid Sci.*, **6**, 162-170 (1951). Gibson, L. J.; M. F. Ashby. Cambridge University Press, Cambridge, UK, 1990

Foam Filling and Curing for Complex Mold





Simpler Model:

- Supports understanding of filling the mold and evolution of the interface
- Model shows density evolution and filling profile over time

Rao et al., "A finite element/level set model of polyurethane foam expansion and polymerization," Computers & Fluids, 2018

Adding Bubble-Scale Information: Population Balance Equations

Governing Equations

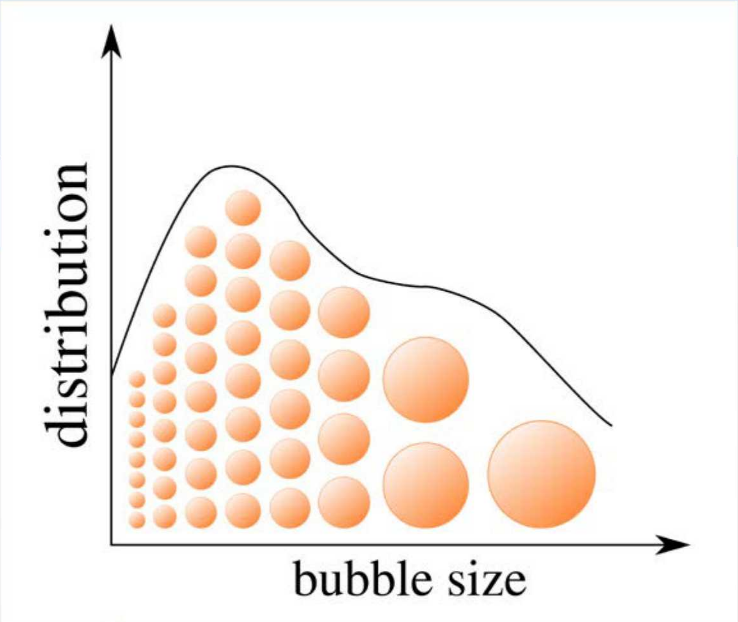
Bubble size distribution (BSD) is described by a number density function, $n(v)$, representing the number of bubbles per unit volume of liquid in volume between the range v and $v + dv$

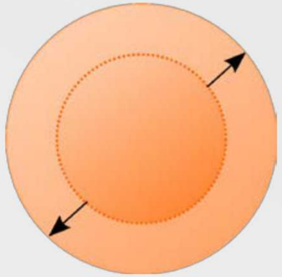
Evolution of the BSD is governed by the following Population Balance Equation

$$\frac{\partial n(v)}{\partial t} + \nabla \cdot (n(v)\boldsymbol{u}) + \frac{\partial}{\partial v}[n(v)G(v)]$$

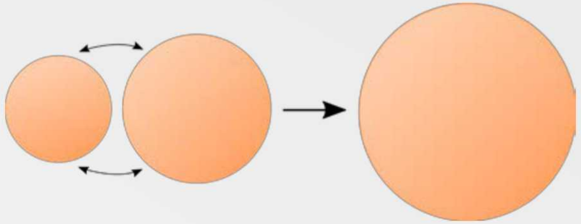
$$= \frac{1}{2}\int_0^v \beta(v', v - v')n(v')n(v - v')dv' - \int_0^\infty \beta(v, v')n(v)n(v')dv'$$

Where $\beta(\mathrm{v}', \mathrm{v})$ represents the coalescence kernel, and $G(v)$ represents the growth rate of bubbles.





Growth Rate Kernel, $G(v)$



Coalescence Kernel, $\beta(v, v')$

References
Karimi et al. 2017, Computer Physics Communications
Karimi et al. 2016 Macromolecular Symposia
Karimi et al. 2017 Computer Physics Communications

Transformation to Moment-Based Transport Equations

$$m_k(t,x) = \int_0^\infty n(v)v^k dv$$

Transformed PBE:

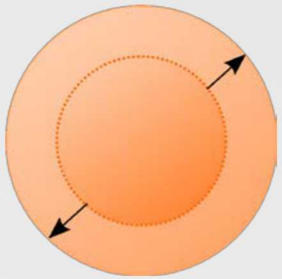
$$\frac{\partial m_k}{\partial t} + \boldsymbol{u} \cdot \nabla m_k = G_k + S_k \,, \qquad k = 0,1,2,3$$

- G_k is a source term relating to the growth rate, and S_k relates to coalescence
- Quadrature method of moments (QMOM) is used to compute the source terms
- Use the first 4 moments to represent our PBE
- Moments offer useful information:

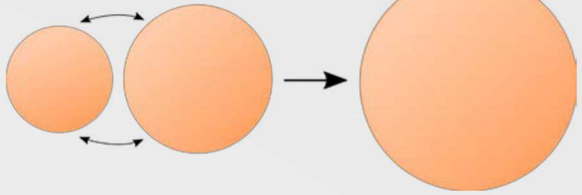
  m_0, total number of bubbles per unit liquid volume

  m_1, total bubble volume per unit liquid volume

  m_2 and m_3 related to the variance and skewness of the BSD



$$\bar{G}_k \cong \sum_{i=1}^{N} w_i G(v_i) v_i^{k-1}$$



$$\bar{S}_k \cong \frac{1}{2}\sum_{a=1}^{N}\sum_{b=1}^{N} w_a w_b\left[(v_a+v_b)^k - v_a^k - v_b^k\right]\beta(v_a,v_b)$$

Volume fraction of gas	Mean bubble diameter
$\frac{m_1}{1+m_1}$	$\left(\frac{m_1}{m_0}\frac{6}{\pi}\right)^{\frac{1}{3}}$

References: Marchisio, Fox 2005 Journal of Aerosol Science, Karimi et al. 2016 Macromolecular Symposia, & Karimi et al. 2017 Computer Physics Communications

Physical Properties of Foam Can Be Related to Moments

We use the first moment, which is the total bubble volume per unit volume of liquid mixture, for calculation of density, viscosity, etc.

$$\psi = \frac{m_1}{1 + m_1}$$

Viscosity is fit using a Taylor-Mooney model

$$\rho_{foam} = \rho_{gas}\psi + \rho_{liquid}(1 - \psi)$$

$$\eta = \eta_0 \exp\left(\frac{\psi}{1 - \psi}\right)$$

$$C_p = \frac{C_{p,liquid}\rho_{liquid}(1 - \psi) + C_{p,CO_2}\rho_{gas}\psi}{\rho_{foam}}$$

$$k = \frac{2}{3}\left(\frac{\rho_{foam}}{\rho_{liquid}}\right)k_{liquid} + \left(1 - \frac{\rho_{foam}}{\rho_{liquid}}\right)k_{gas}$$

Two-Phase Kinetics Formulation with Bubble-Size Information

$$\frac{\partial C_{H_2O}}{\partial t} + \boldsymbol{u} \cdot \nabla C_{H_2O} - D_{H_2O} \nabla^2 C_{H_2O} = -N k_{H_2O} C_{H_2O}^p$$

$$\frac{\partial C_{CO_2}^{liq}}{\partial t} + \boldsymbol{u} \cdot \nabla C_{CO_2}^{liq} - D_{CO_2}^{liq} \nabla^2 C_{CO_2}^{liq} = N k_{H_2O} C_{H_2O}^p - \bar{G}_1 \frac{P}{RT}$$

$$\frac{\partial C_{CO_2}^{gas}}{\partial t} + \boldsymbol{u} \cdot \nabla C_{CO_2}^{gas} - D_{CO_2}^{gas} \nabla^2 C_{CO_2}^{gas} = \bar{G}_1 \frac{P}{RT}$$

To account for growth rates of bubbles we have equations for both concentrations of liquid CO_2 and gaseous CO_2 and relate these based on growth rate determined by the QMOM

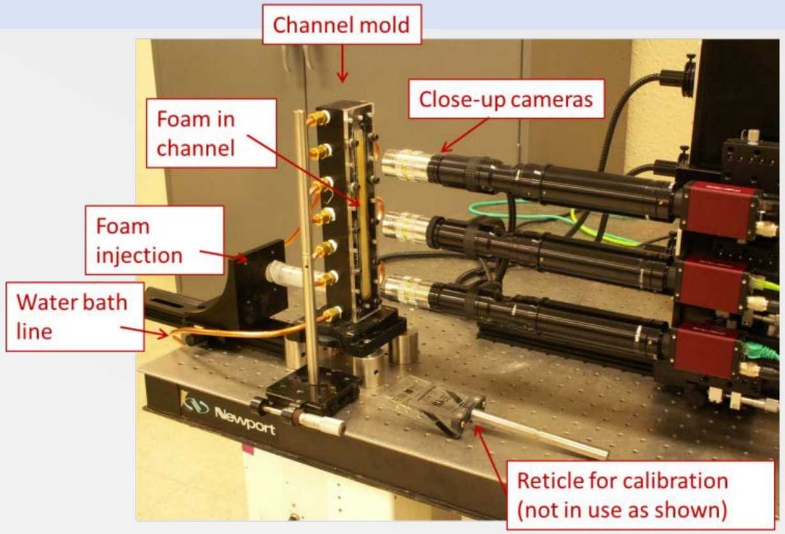
$$\bar{G}_k \cong \sum_{i=1}^{N} w_i G(v_i) v_i^{k-1}$$

$$G(v_i) = G_0 (w_{CO_2} - w_{max}) / w_{max}$$

Where w_{CO_2} and w_{max} are mass fraction of liquid CO_2 and mass fraction related to the maximum solubility of liquid CO_2

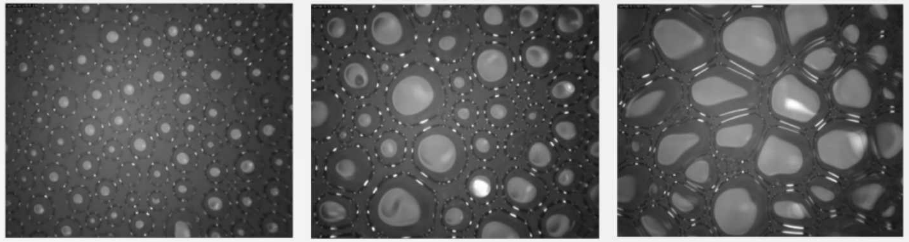
$\bar{G}_1$ is the source for m_1 (total bubble volume per unit liquid volume)

Experimental Setup: Study of the Evolution of Bubble Size

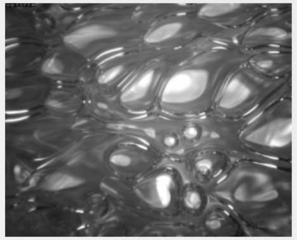


- Three cameras record bubbles at transparent wall (top, middle, and bottom of a column) as foam fills the column
- Light area in pictures below are where the wall is wetted by the bubble – edges are dark lines dashed with bright spots (makes difficult to automatically analyze)
- Image processing developed to analyze – checks by hand shows software good until late times when the bubbles distort severely
- Bubbles nominally about 200-300 microns in diameter
- Size and shape evolve in time, depend on temperature, foam density
- Over packing the foam helps keep the bubbles small and round
- Under packed foam often ends up with highly distorted bubbles near leading front

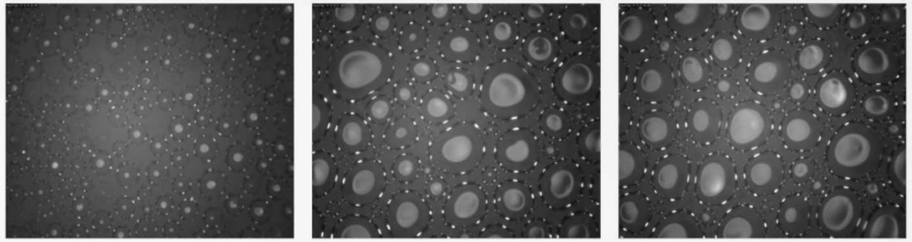
PMDI-4 free rise (bottom camera)



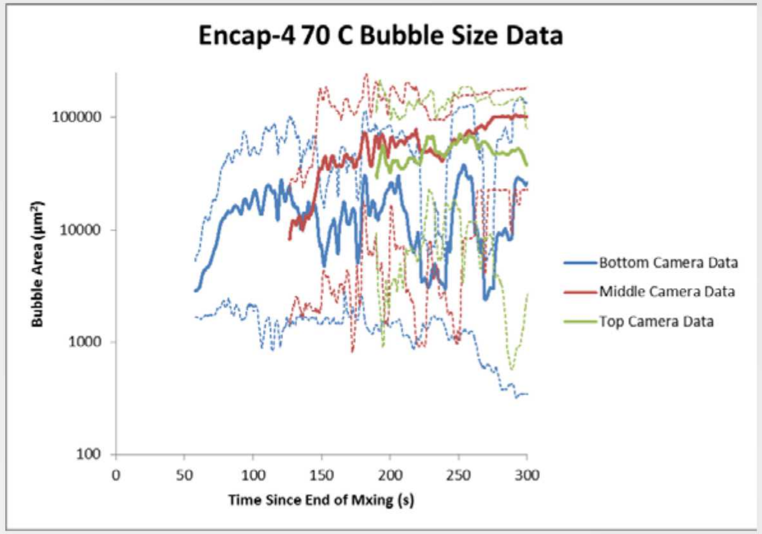
Top free rise



PMDI-4 packed to 8pcf (bottom camera)



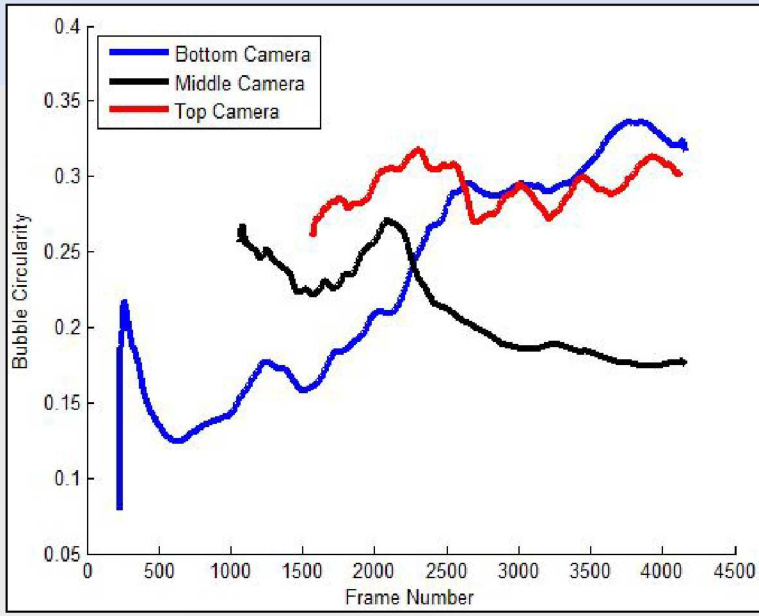
Time=79.5 s   Time=152 s   Time=266 s since end of mixing



Results of image processing. Solid lines are mean value. Dotted lines indicate top and bottom 10% of values to indicate spread.

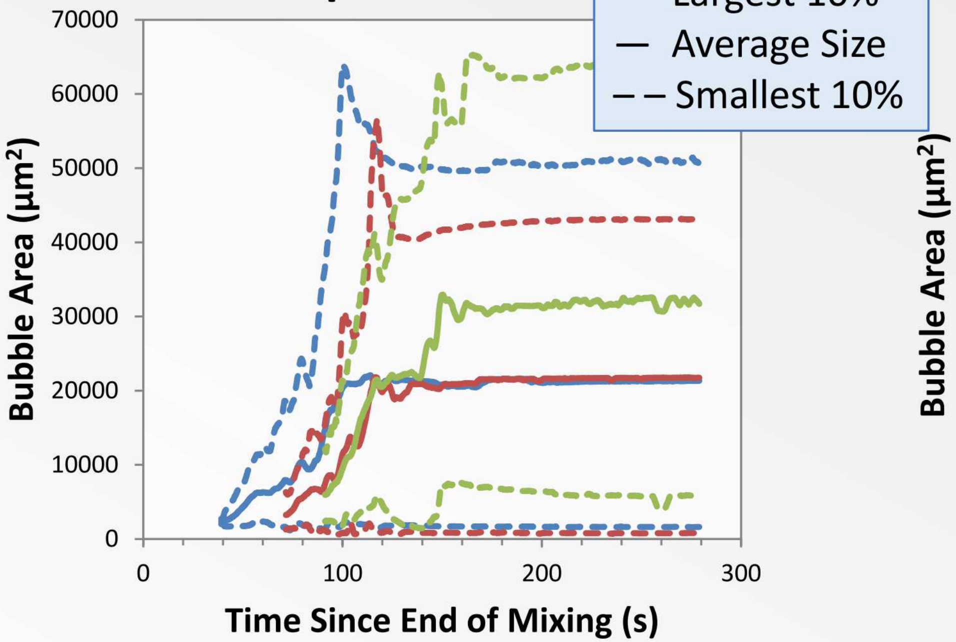
Roberts et al. 2016 SAND2016-5445

Sample Uniformity: Distribution of Bubble-Size from Top to Bottom

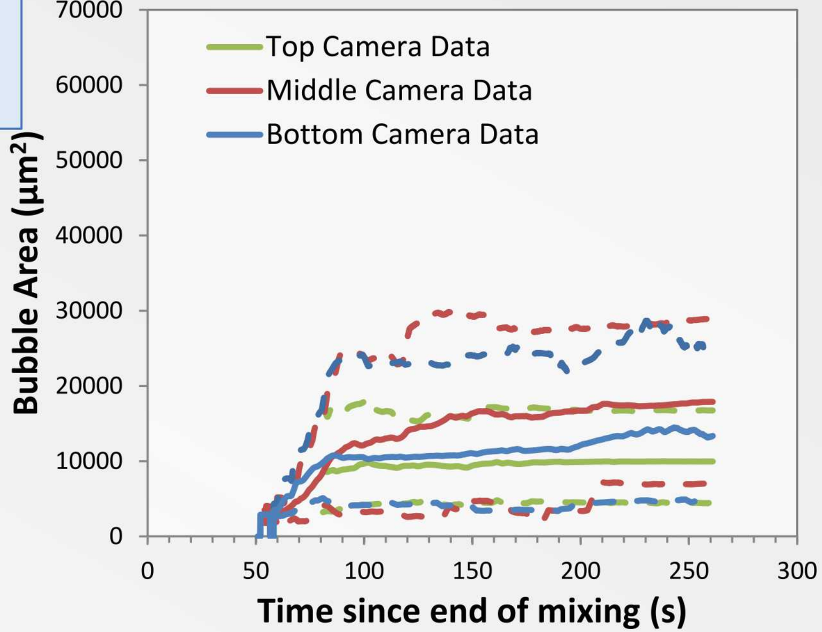


- Bubbles are first observed at the bottom camera, then middle and top as the foam rises in the channel.
- In general, bubbles at the top of the channel tend to be larger than those at the bottom due to creaming. In other cases, the bubble distribution is fairly uniform.
- The size distribution of bubbles broadens as the bubbles grow.
- Bubbles become less spherical with time due to shear with the channel wall

Encapsulation foam, 70 °C
Over-packed to 8

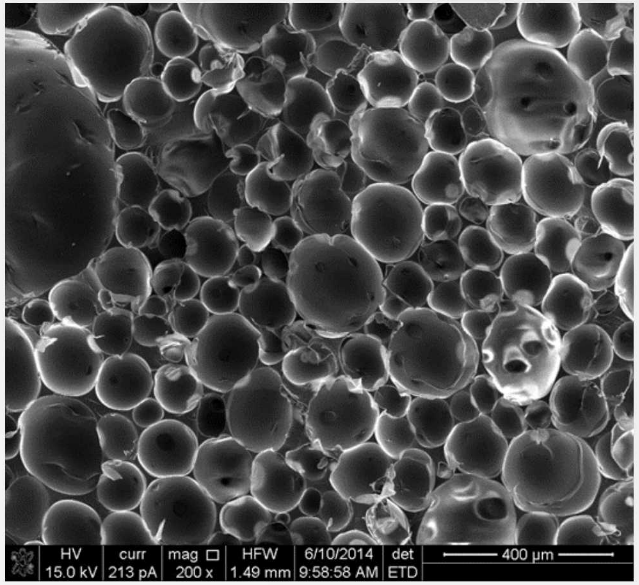


Structural foam, 40 °C
Over-packed to 20 lb/ft³

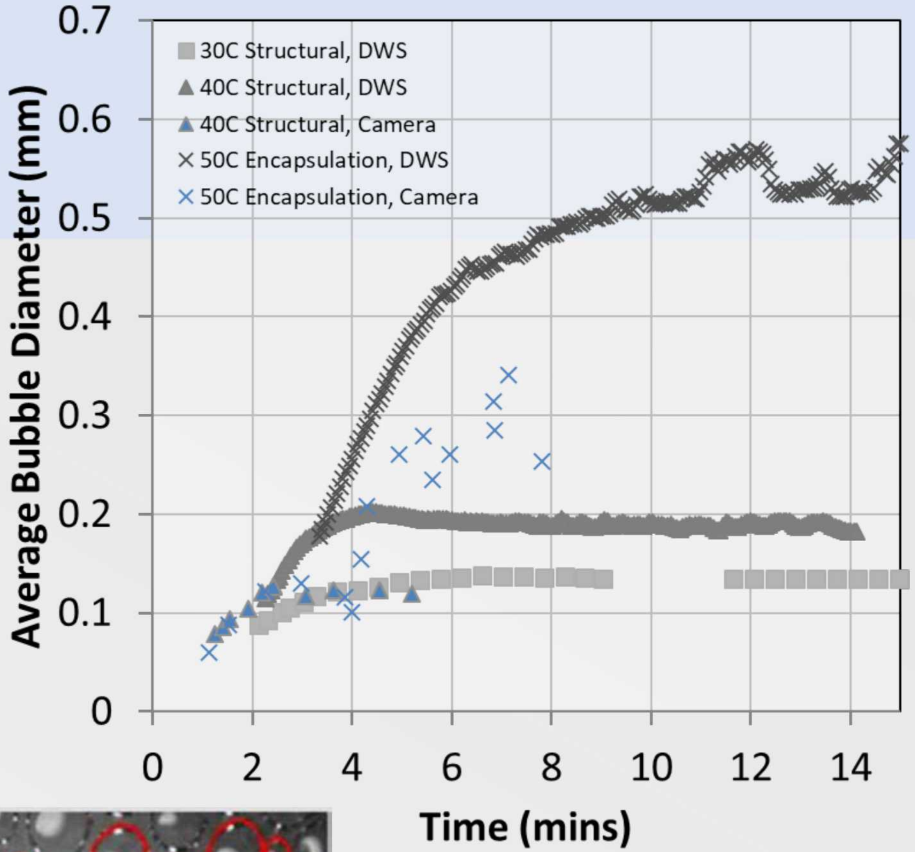


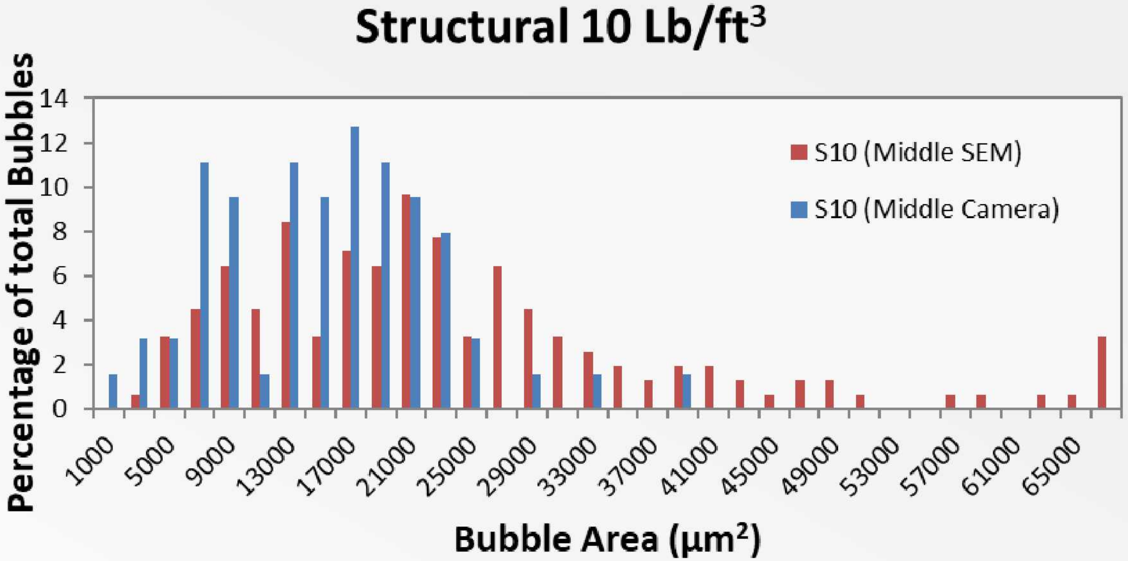
The mean circularity of the bubbles, in PMDI-4 foam for restricted free rise, as defined by $(r_{max} - r_{min})/ r_{avg}$ This gives zero for a perfect circle and > 0 for oblong shapes

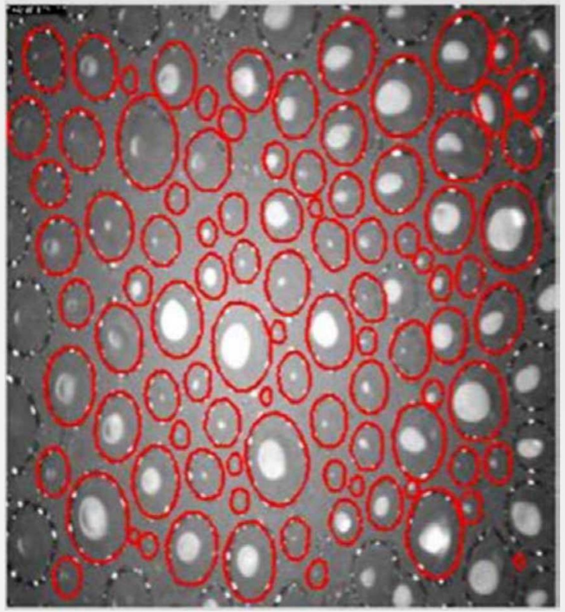
Comparison of Methods



- Scanning electron microscope images show a slightly larger bubble size than the optical method.
- This is because bubbles tend to be smaller at the wall.
- All methods trend well together



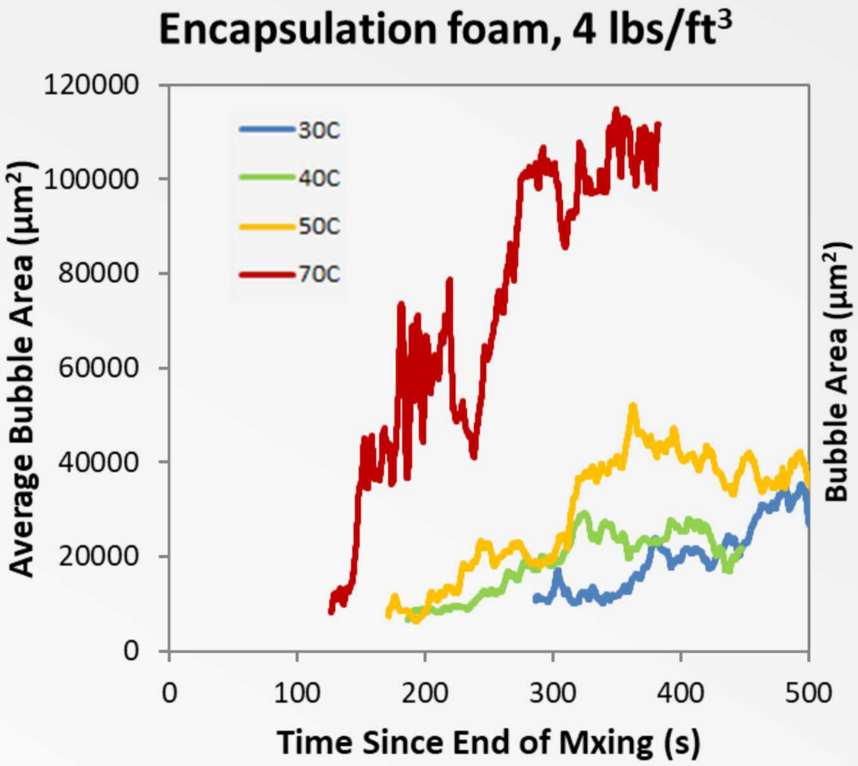


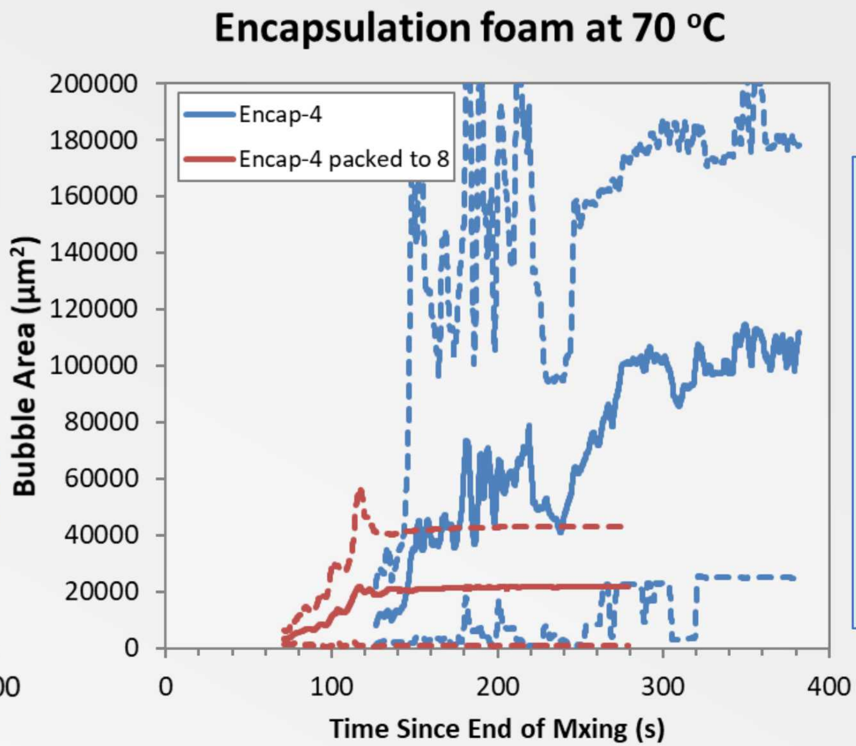


- MATLAB script counts bubble-size evolution over time
- SEM just measures final bubble size

Effect of Temperature and Pressure on Bubble Size

- Bubbles are larger and grow faster when the oven temperature is higher due to both faster reaction rates and lower gas density.
- Overpacking the foam in the channel results in smaller, more uniform bubbles.





- Over-packing creates a more dense foam.
- Pressures (not shown) are also higher for over packed foam.
- Higher temperatures lead to larger bubble size

Initial Fitting of Bubble-Size Distribution to 0-D Model

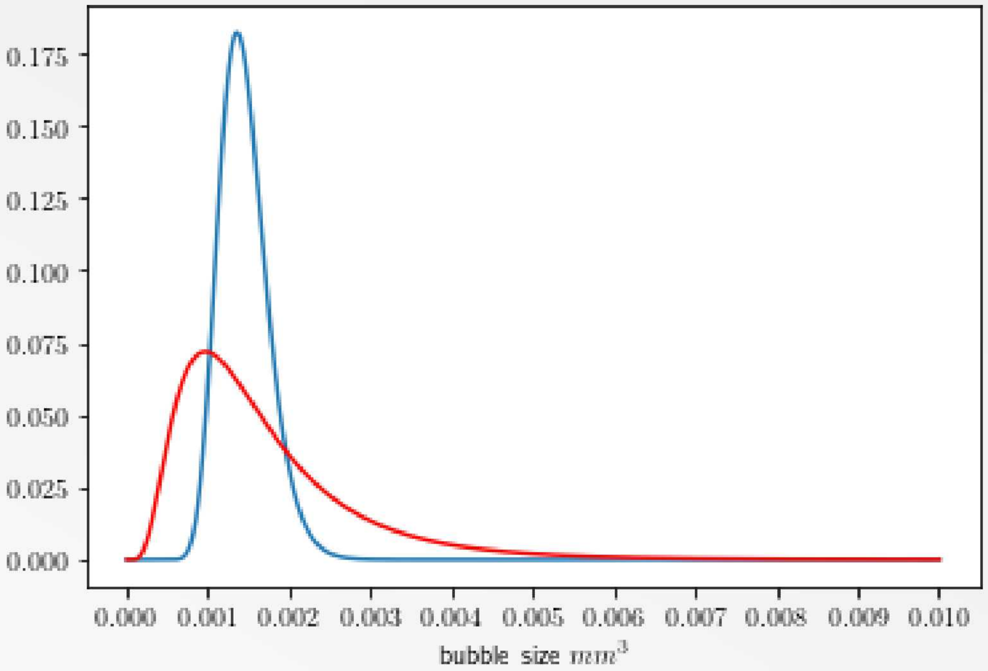
- For initial values and distribution information we fit the BSD information from Roberts et al. to a 0-D version of our model
- Following Ferkl et al. 2016 we initialized our moments to a log-normal distribution

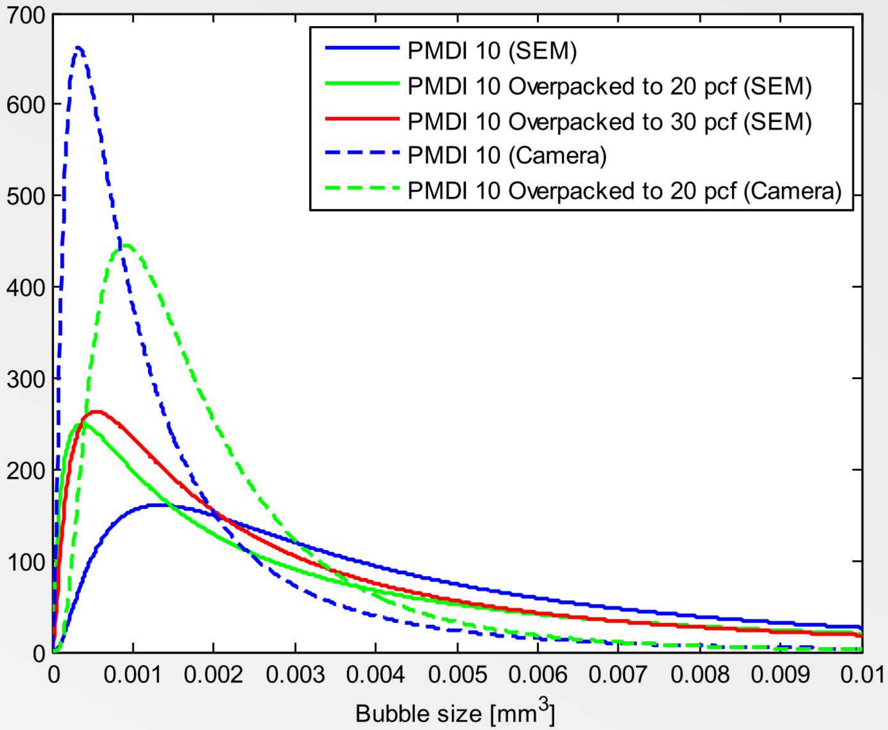
$$m_k = \frac{v_0 n_0 exp(k\ log(v_0) + 0.5k^2\sigma^2)}{exp(log(v_0) + 0.5\sigma^2)}$$

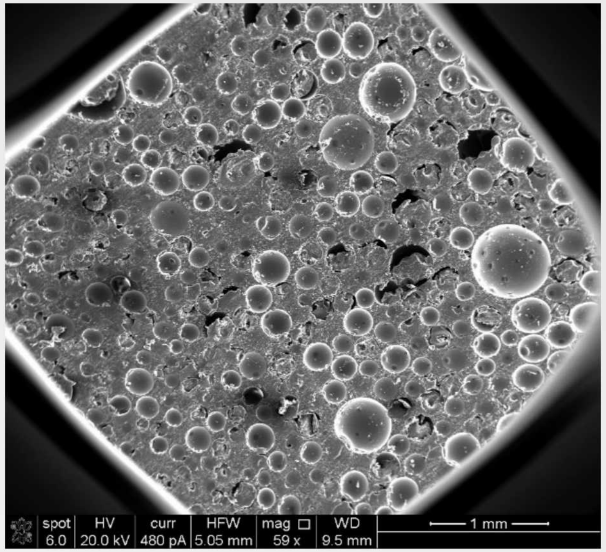
- Where
- v_0 corresponds to a mean volume in our initial BSD
- n_0 corresponds to the initial number density
- σ is the usual log-normal σ relating to the variance of our initial distribution

Initial Fitting of Bubble Size Distribution to 0-D Model

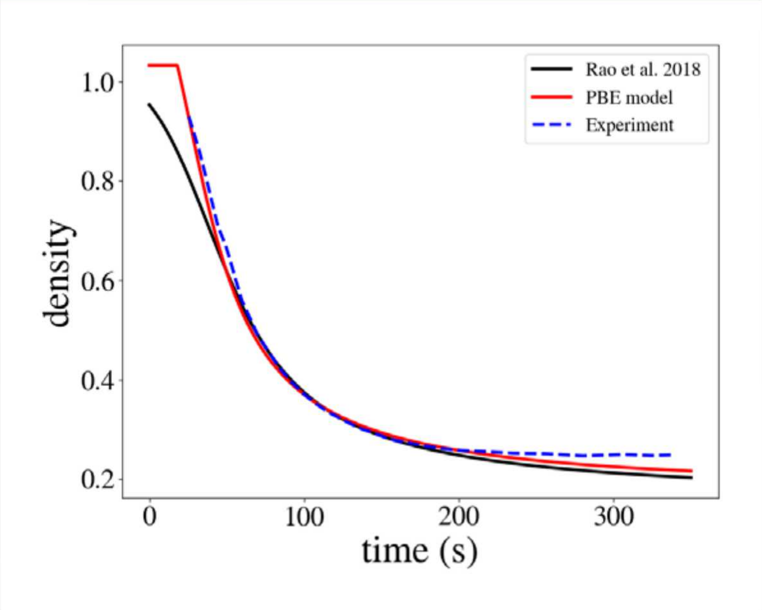
- Distribution is recovered assuming a log-normal distribution using method described by John et al. 2007
- Current distribution does not match as well as we would like
- Need to explore more robust fitting methods



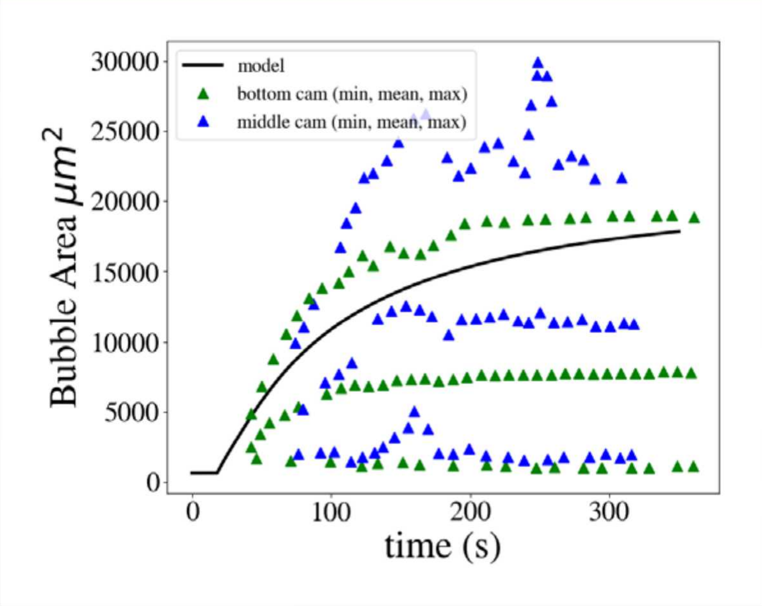




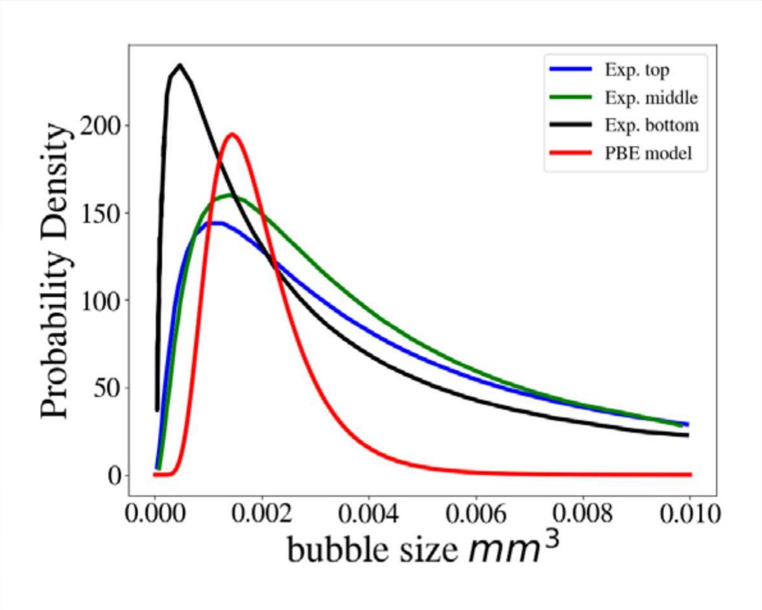
Initial fitting using a 0-D model and Karimi Model



Our initial density fits reasonably well with experimental data



Our bubble area appears to be within the range found by experiment

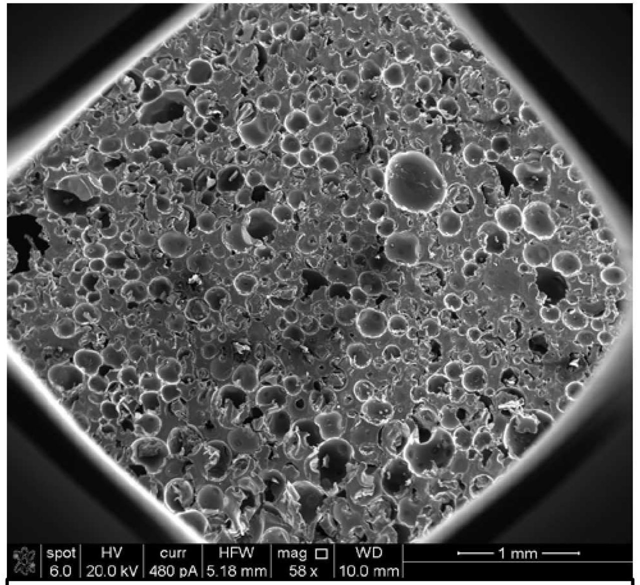


Our bubble size distribution is around the same range though we are lacking the longer tail.

Our recalculation of distribution from moments is not very robust

Improvements to PBE-QMOM Foam Model

- Initial model based on linking our kinetics with Karimi PBE-QMOM model could not simultaneously fit density and bubble size distribution
- New bubble growth kernel to account for decreased growth with increasing viscosity
- New coalescence kernels was added to account for bubble size and polymerizing viscosity
- With these changes, we were able to fit experimental data well.



SEM near middle of bar

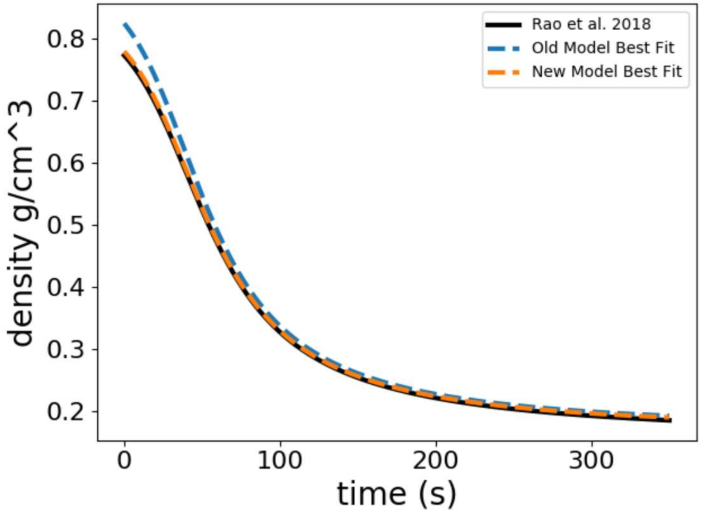
Population balance equation, which is solved using QMOM:

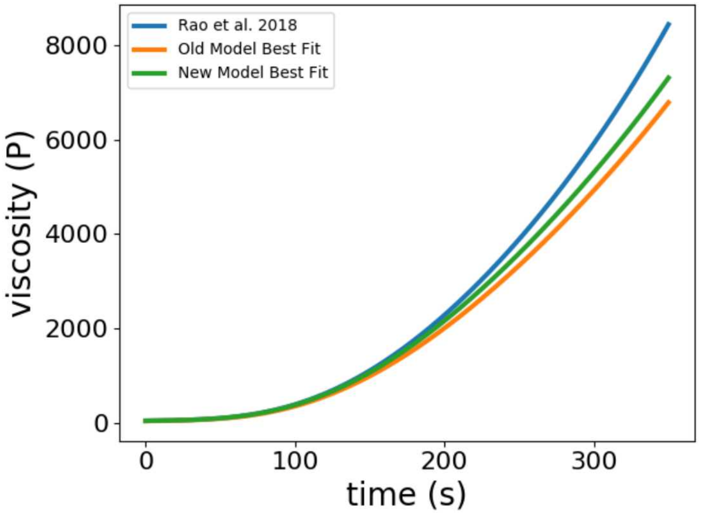
$$\frac{\partial n(v)}{\partial t} + \nabla \cdot (n(v)\boldsymbol{u}) + \frac{\partial}{\partial v}[n(v)G(v)]$$

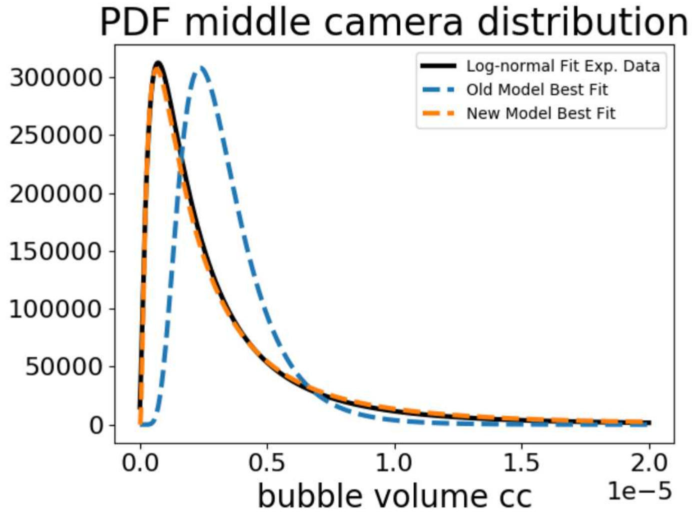
$$= \frac{1}{2}\int_0^v \beta(v', v - v')n(v')n(v - v')dv' - \int_0^\infty \beta(v, v')n(v)n(v')dv'$$

$\beta(\mathrm{v}', \mathrm{v})$ isthe coalescence kernel, and $G(v)$ represents the growth rate

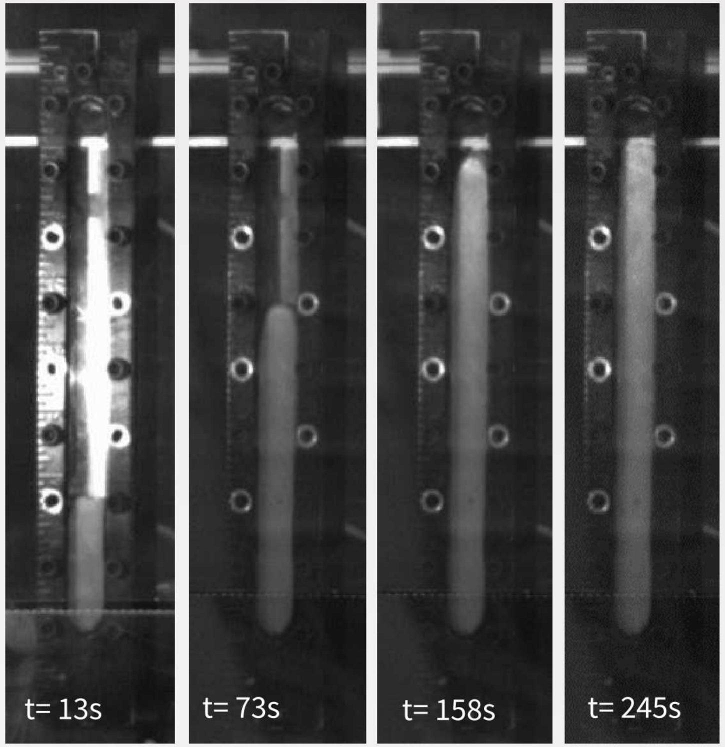
	Old Model	New Model
$G(v)$	$C_0\left(\max\left(0, \frac{w - w_{max}}{w_{max}}\right)\right)$	$C_0\frac{\mu_{ref}}{\mu}\left(\max\left(0, \frac{w - w_{max}}{w_{max}}\right)\right)$
$\beta(v', v)$	$\beta_0(v + v')$	$\beta_0\frac{\mu_{ref}}{\mu}(v + v')\max\left(\frac{v}{v'}, \frac{v'}{v}\right)$



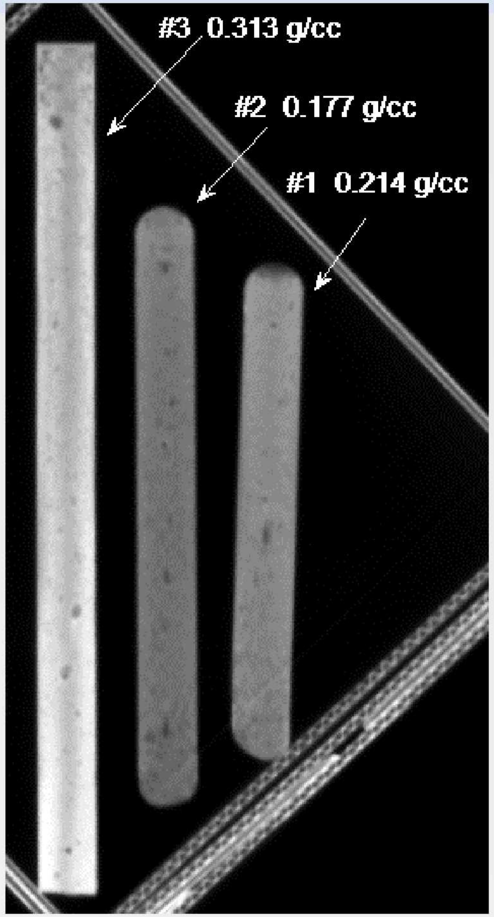




Density Study for Structural Foam PMDI-10



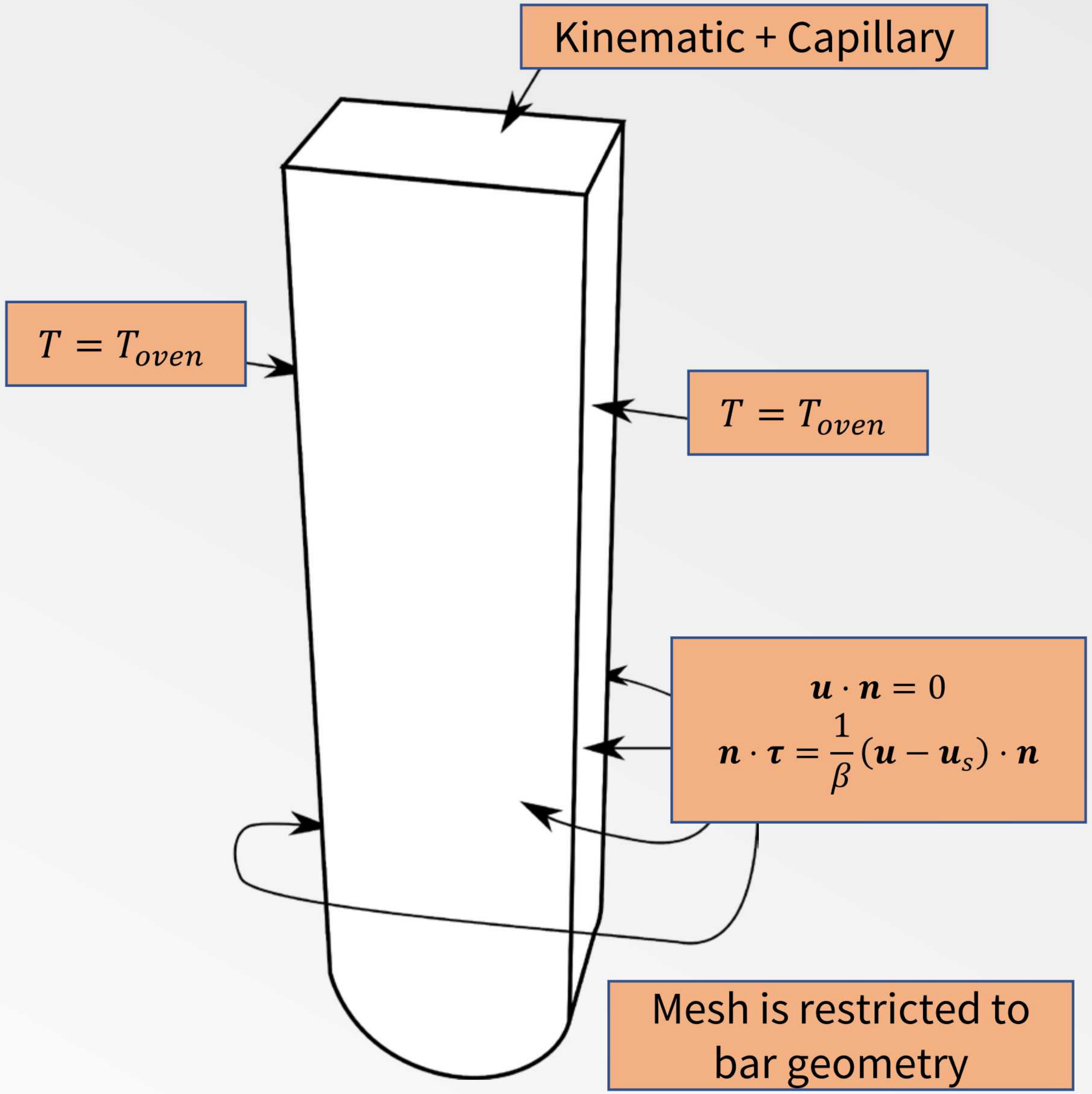
Foam expanding in a mold at 30°C. Time shown on frames is after the end of mixing the resin and the curative together for 45 seconds.



X-ray image of PMDI-10 foam bars: 1) free rise at 30°C, 2) free rise at 50°C, 3) over packed (1.5) at 30°C

- Can the model predict the effects of over packing seen experimentally?
- Over-packed sample shows higher density and greater density variation
- 17% for free rise and 31% for over-packed foam bars

Problem Setup Foam Bar



- Q1 8-node Hex elements
- PSPG + SUPG stabilization on momentum and continuity
- SUPG stabilization on species and moment equations
- Some surface tension is used to stabilize the interface

Boundary Conditions (BCs)

- Sides have no penetration condition
- Surface tension is applied to stabilize the interface
- A Navier-slip condition is applied on the edges to allow the foam to slip
- Sides are set to the oven temperature

Mesh BCs

- Mesh is restricted to not leave initial plane on sides
- Kinematic BC is applied on top and the surface is allowed to move in Lagrangian manner
  - $(\boldsymbol{u} - \dot{\boldsymbol{x}}) \cdot \boldsymbol{n} = 0$

Other BCs

- Bottom curved surface (not shown) is restricted so that velocity is zero and the mesh does not move

Interface Tracking

Arbitrary Lagrangian Eulerian (ALE) Method

Boundary fitted pseudo-solid approach is used, deformation occurs due to motion at free surfaces

$$\nabla \cdot \boldsymbol{S} = 0, \qquad \boldsymbol{S} = \lambda_s e\boldsymbol{I} + 2\mu_s \boldsymbol{E}$$

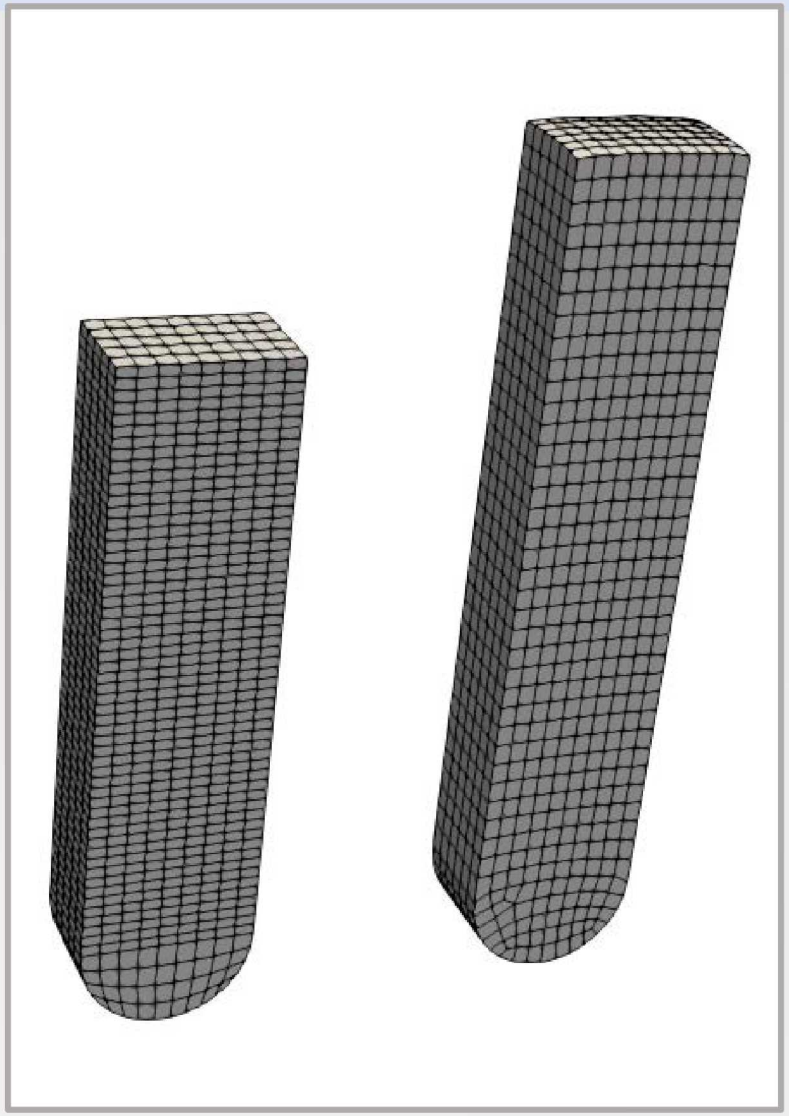
$\boldsymbol{S}$ is the Cauchy stress in the pseudo-solid.

Interface

The interface we track is the foam liquid-air interface.

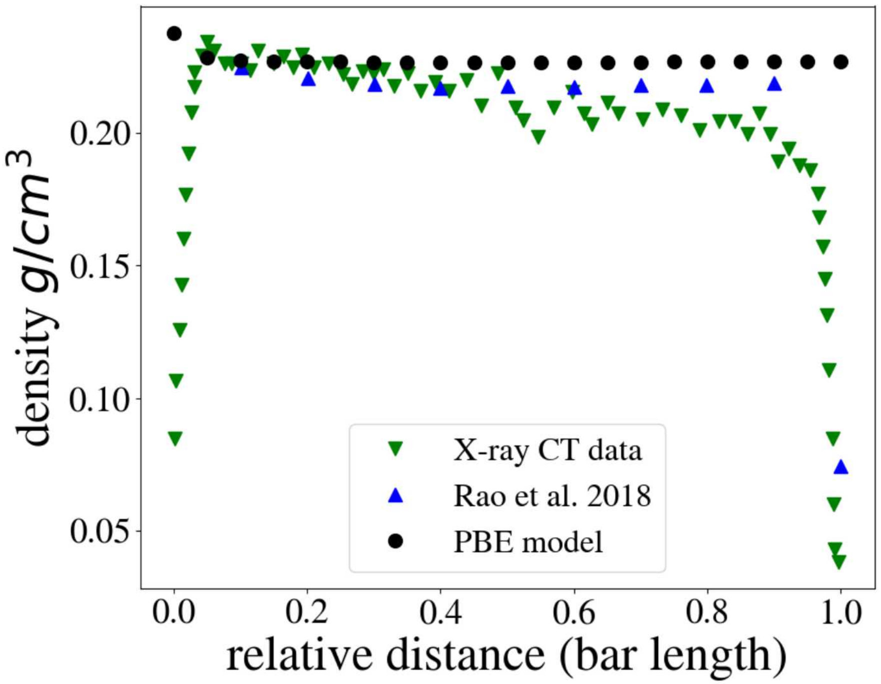
We ignore all physics in the air and only track the foam phase

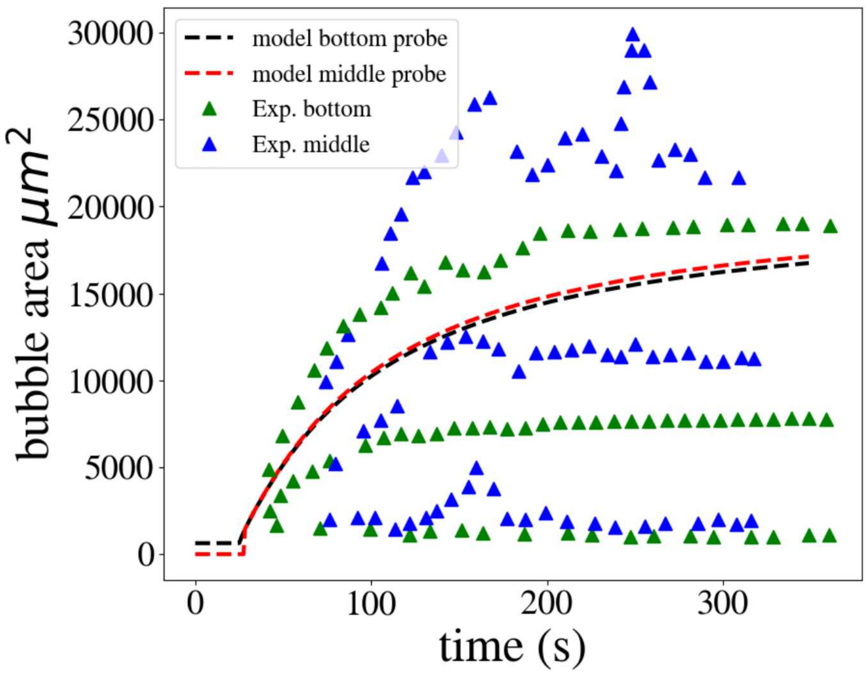
Remeshing is done after a set number of timesteps to avoid low quality elements

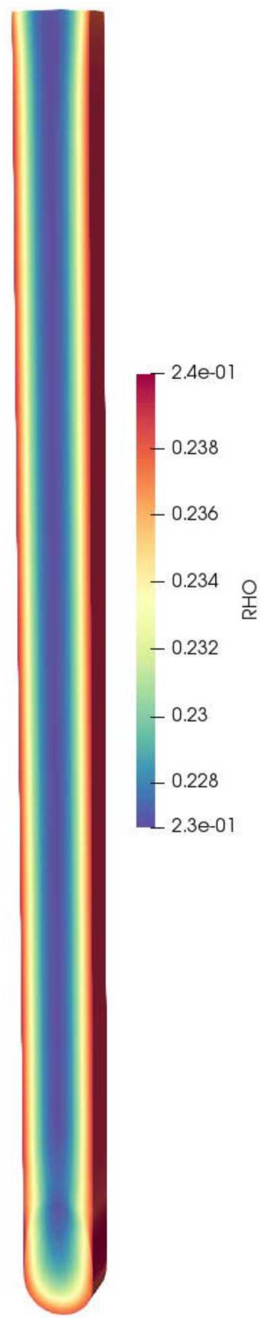


Reference: Sackinger et al. 1996 *J. Comp. Phys.*

3D ALE Bar Modeling Results







Conclusions and Future Work

- We have a mature engineering model for polyurethane
- We have added a population balance method to predict bubble size distribution
- We have improved the population balance method with new coalescence and growth kernels. We think a nucleation kernel would also be useful.
- We are testing this methodology on foam data, for which we have more characterization and bubble size data from various methods including optical, SEM, X-Ray μCT, and DSW
- We are now applying this coupled CFD-PBE model to more complex geometries and adding an adaptive meshing capability to help stabilize the hyperbolic and poorly behaved moment equations